

Diffusive Growth of a Polymer Layer by *In-Situ* Polymerization

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We consider the growth of a polymer layer on a flat surface in a good solvent by *in-situ* polymerization. This is viewed as a modified form of diffusion-limited aggregation without branching. We predict theoretically the formation of a pseudo-brush with density $\phi(z) \propto z^{-2/3}$ and characteristic height $H \propto t^3$. These results are found by combining a mean-field treatment of the diffusive growth (marginally valid in three dimensions) with a scaling theory (Flory exponent $\nu = 3/5$) of the growing polymers. We confirm their validity by Monte Carlo simulations.

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Polymer brushes (layers of linear polymer chains end-grafted to a surface) find use in the stabilization of colloidal particles in solution [1]. One way to form these layers is by adsorption of pre-existing polymers having a functionalised group on one end, but this process turns out to be extremely slow for high grafting densities [2]. An alternative is the polymerization of a brush *in situ*; brushes formed this way have been reported, but not characterized in detail [3]. In this paper we study an idealized model of in-situ growth of a layer, in which a flat impenetrable surface is initially densely covered with initiator sites. From these seeds, linear unbranched chains can grow by irreversible polymerization, with monomers added only at chain ends. The chains so formed are treated as *flexible coils*: they can relax their structure in response to excluded-volume interactions with their neighbours. This process sets a dynamical time scale; we restrict attention to slow enough growth, such that local equilibrium is maintained at all times. We also assume a constant diffusivity for the free monomers and a constant, infinitesimal flux of incoming random walkers. (For a finite, or a time-dependent, incident flux, our description breaks down, as discussed later.)

The above-formulated problem of *in situ* polymerization is closely related to that of DLA (Diffusion-Limited Aggregation [4]) without branching [5,6,8,9]. There is no satisfactory mean-field formulation for ordinary DLA [4,10], but a continuum field approach does exist to describe the growth of a forest of needles by diffusive deposition, with adsorption on the

needle-tips only [8]. It was found by simulation [5] that the mean-field calculation is rather accurate in $d = 3$ dimensions, and later realized [9] that this is the upper critical dimension for the problem, so that only logarithmic corrections to the mean-field results should apply. In what follows, we generalize the needle growth model to a much wider class of processes, in which there is an arbitrary power-law exponent ν defined by $\phi(z) \sim \xi(z)^{1/\nu-d}$ where $\phi(z)$ is the density at height z and $\xi(z)$ the associated transverse separation between linear growing objects. (This is the usual relation, for an object of fractal dimension $1/\nu$, between the density and a “blob size” which is locally given by the separation $\xi(z)$.) For *in-situ* polymerization in a good solvent, ν is simply the usual Flory exponent $\nu = 3/5$ [12]. In this case, we predict the formation of a novel power-law “pseudobrush” [13] in which chains are extremely polydisperse but, nonetheless, strongly extended from the surface: the density of grafted material decays with a power law of height, $\phi(z) \propto z^{-2/3}$, and the spacing between chains at height z varies as $\xi \sim z^{1/2}$. We have tested these predictions by Monte Carlo simulation using the bond-fluctuation model (BFM) [14]. Good agreement is obtained in $d = 3$, which remains the upper critical dimension for any ν (as may be confirmed by a simple reworking of Krug’s argument [9]).

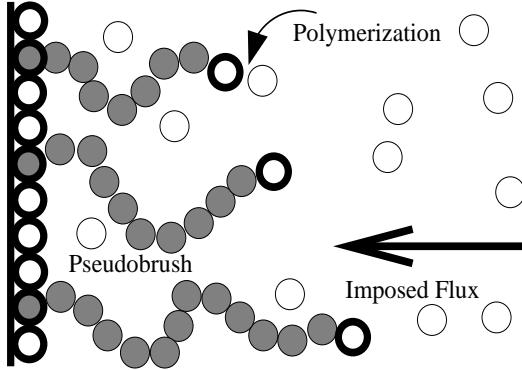


FIG. 1. Sketch of diffusive growth of a polymer layer by *in situ* polymerization.

The continuum field description of the growth can be formulated quite simply. We define three coarse-grained densities (each expressed as a local volume fraction): (i) that of the aggregated monomers $\phi(z, t)$; (ii) that of active end monomers $\rho(z, t)$; and (iii) that of free monomers $u(z, t)$. These are coupled by three differential equations, as follows. Firstly, we suppose the polymerization is a local second-order process:

$$\partial_t \phi = k u \rho \quad (1)$$

where k is a reaction constant. Secondly, conservation of the particles implies:

$$\partial_t \phi = -\partial_t u + D \Delta u = D \Delta u \quad (2)$$

where D is the diffusivity of free monomers. The second equality embodies the “adiabatic” approximation, valid in the quasi-static limit of infinitesimal flux [4]. Thirdly we have a “constitutive relation” between local monomer density ϕ and blob size, or equivalently between ϕ and the end density, ρ :

$$\rho = -l \partial_z \phi^{1/\epsilon} \quad (3)$$

Here l is of order of the monomer size, b . This relation arises because the number of chains $\mathcal{N}(z)$ per unit area of surface surviving to height z is (by simple geometry) of order $\xi(z)^{1-d} \simeq \phi^{(1-d)/(1/\nu-d)}$, and the end density is $-\partial\mathcal{N}/\partial z$. Hence ϵ obeys $\epsilon = (d-1/\nu)/(d-1)$. Within this continuum approach, the exponent ϵ contains all required information about local chain structure. Adopting Flory's estimate, $\nu = 3/(2+d)$, we have $\epsilon = 2/3$ (which is, by accident, independent of d).

Next we consider the boundary conditions. Within the continuum model, as we show below, the density of adsorbing chain ends is (formally) divergent near the wall, so the chance of an incident particle actually reaching the wall is negligible. We thus require that the density of the free monomers, and its gradient, vanish there:

$$u(0, t) = \partial u(0, t)/\partial z = 0. \quad (4)$$

Secondly, the boundary condition on u at infinity is that appropriate to a (small) constant flux j_∞ of incoming monomers (each of volume b^d):

$$\lim_{z \rightarrow \infty} \partial u(z, t)/\partial z = b^d j_\infty / D \equiv g_\infty. \quad (5)$$

This ensures (in the adiabatic limit) that the mass of the layer grows linearly in time. For convenience, we may set $1/k = l = 1$ by choosing these as the units of time and length. Two parameters then remain, the reduced flux g_∞ and the reduced diffusivity $D/kl^2 = D$. The latter may itself be set to unity by the rescalings $\phi = D^\epsilon \tilde{\phi}$, $\rho = D\tilde{\rho}$, $u = D^{\epsilon-1}\tilde{u}$ and $g_\infty = D^{\epsilon-1}\tilde{g}_\infty$. In what follows we suppress the tildes (i.e. we choose $D = 1$) but restore the scale factors later as required.

We now define a characteristic layer height by the first moment [11] $H(t) = \int z\phi dz / \int \phi dz$, and seek solutions of Eqs.(1-5) in terms of the scaled variable $x = z/H(t)$:

$$\phi = z^{-\alpha} f(x) ; \quad \rho = z^{-\beta} h(x) ; \quad u = z^\gamma g(x) \quad (6)$$

Consistency of this scaling ansatz with the governing equations and the boundary conditions fixes the exponents α, β, γ as we now show. Firstly, we eliminate $\partial_t \phi$ from Eqs. (1, 2) to obtain $u\rho = \partial_z^2 u$. This forces the end-density to decrease with an exponent $\beta = 2$. Secondly, the constant flux boundary conditions, eqns. (4,5) impose an exponent $\gamma = 1$ (with $g(\infty) = g_\infty$ and $g(0) = 0$). Finally, we require on physical grounds that the function $f(x)$ approaches a finite limit at the origin, and that $f(\infty) = 0$. The constitutive relation eq. (3), between monomer and absorber density then reads $\epsilon z^{-\beta} h(x) = z^{-(1+\alpha/\epsilon)} f(x)^{1/\epsilon} (\alpha - x(\ln f(x))')$ where the prime denotes a derivative. Equating powers of z we obtain $\beta = 1 + \alpha/\epsilon$; within mean field theory ($\beta = 2$), this implies $\alpha = \epsilon$ which fixes our final exponent. It follows immediately that $\xi \propto z^{1/(d-1)}$, and hence $\xi \propto \sqrt{z}$ in 3 dimensions; this result is independent of ϵ . In contrast, the total mass $M = \int_0^\infty \phi(z) dz$ obeys $M = \eta H^{1-\epsilon}$ where $\eta(\epsilon) = \int_0^\infty x^{-\epsilon} f(x) dx$. Under constant flux conditions, $M = g_\infty t$, and one has accordingly $H(t) = (g_\infty t / \eta)^{1/(1-\epsilon)}$. This completes, at the scaling level, the generalization of the mean field theory for needle growth ($\epsilon = 1$) [8] to the case of arbitrary ϵ . Note that, at this level, the only difference between the needle model and the case of general ϵ lies in the fact that, when a particle is adsorbed, the adsorbing end moves forward by one monomer size for needle growth but less than this for the polymer case. Since only the active ends participate in screening, the scaling $\rho \sim z^{-2}$ remains as for needles, and $\beta = 1 + \alpha/\epsilon$ then follows from Eq.3.

To test these predictions, we have performed detailed bond-fluctuation model simulations (for the method, see [14]). In this athermal model, “local jumps” are made by choosing one monomer at random (regardless of whether or not it is part of a chain) and attempting to jump one lattice unit in a randomly chosen basis direction. The attempt is accepted if excluded volume and chain connectivity requirements are satisfied. If a free monomer happens to touch the wall at $z = a$ (a is the lattice spacing) it adsorbs and becomes reactive. A free monomer can polymerize at a reactive chain end whenever the difference vector of the two monomers is an allowed intrachain bond. The simulation box is of size $L_x = L_y = 100a$, $L_z = 500a$ with periodic boundary conditions in x - and y -directions and impenetrable walls at $z = a$ and $z = L_z$. The flux used was $j_\infty = 1.3 \cdot 10^{-7}/\tau a^2$ where τ is the time for one Monte Carlo step per monomer. No hydrodynamic interactions are taken into account. In the adiabatic limit of interest, chains are fully relaxed and the precise dynamics should be irrelevant.

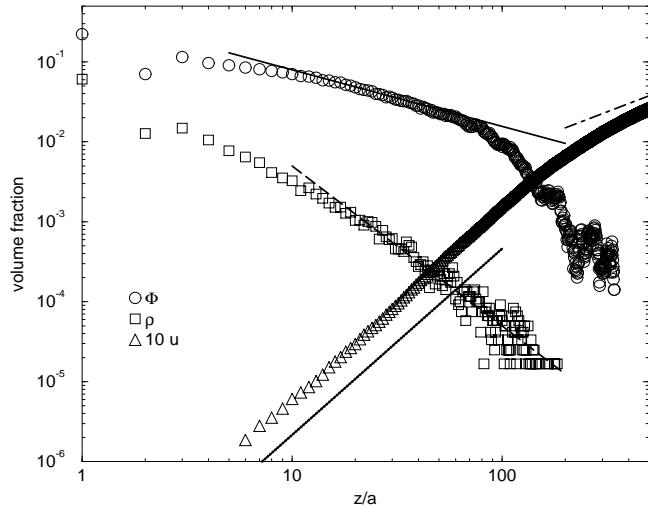


FIG. 2. The density profiles for the grafted monomers ϕ , the end monomers ρ and the free monomers u versus distance z from the wall. An incident flux of $j_\infty = 1.3 \cdot 10^{-7}/\tau a^2$ was imposed over a period of $4 \cdot 10^6 \tau$. We compare the densities with the power law predictions $\alpha = \epsilon = 2/3$ (solid line), $\beta = 2$ (dashed line) and $\gamma = 1$ (dashed-dotted line). Near the wall the density of free monomers increases with distance as $u(z) = zg(x) \sim z^{3-\epsilon}$ (dotted line) corroborating $\gamma = 1$ and the asymptotic power law solution of eq.(7) for small x [15]. The free monomer density (calculated from the incoming free monomer flux) is very small and is vertically shifted.

The density profiles for the grafted monomers ϕ , the end monomers ρ and the free monomers u are shown in fig. 2 and confirm broadly the scaling predictions. In fig. 3 the scaling functions $g(x)$ and $f(x)$ are shown. The direct verification of the scaling prediction for the monomer density is less successful than for the free monomer density. The accuracy of $f(x)$ is roughly indicated by the size of the wiggles, which apparently arise from statistical noise: the accuracy decreases with both x and t , as the density becomes very low. Also, the interactions of the first blobs with the wall and fluctuations near the outer brush-edge,

omitted from our course-grained description, imply two additional length scales (the sizes of the first and the last blob of the layer) which, judging from fig. 3 (b), are non-negligible even at our longest times.

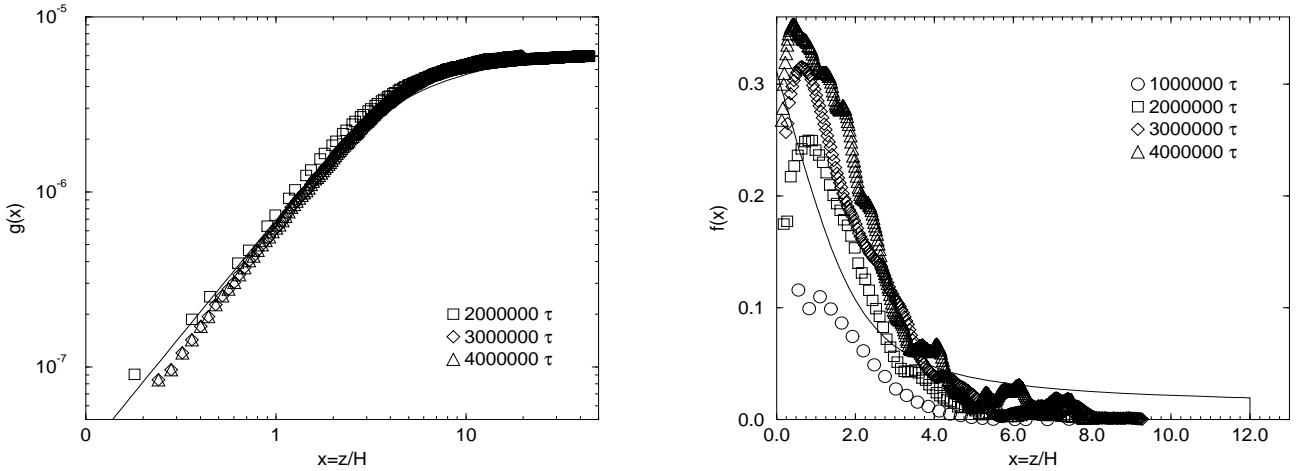


FIG. 3. The scaling functions (a) $g(x)$ and (b) $f(x)$ for several times. The solid line indicates the numerical solution of eq. (7), with a discontinuity at $x_c = 12$, obtained by a Runge-Kutta method. (a) The data collapse justifies the scaling ansatz eq. (6) with an exponent $\gamma = 1$. (b) For $t = 10^6\tau$ the grafted chains are not stretched. As the layer becomes more brush-like the curves merge.

We now return to the scaling functions $f(x)$, $g(x)$ and $h(x)$. Defining a dimensionless parameter $\mu = \frac{g_\infty}{(1-\epsilon)\eta}$ the mean-field equations (1-5) can be reduced to the form:

$$\begin{aligned} h(x)g(x) &= -\mu x^{2-\epsilon}f' = g(x)f(x)^{1/\epsilon} \left(1 - \frac{xf'(x)}{\epsilon f(x)}\right) \\ &= x(2g'(x) + xg''(x)) \end{aligned} \quad (7)$$

These equations (combined with the boundary conditions) determine in principle the scaling functions f, g, h ; they represent a powerful extension, to arbitrary $\epsilon < 1$, of the existing results for needle growth ($\epsilon = 1$). For the latter case, an exact solution of the equations has in fact been obtained [8]. For $\epsilon < 1$, however, we have found numerically (and shown analytically [15]) that no acceptable solutions satisfy the boundary conditions on f . This suggests that either the scaling ansatz is wrong (which seems unlikely, in view of the simulation data shown above), or that new physics intervenes. The latter may certainly be true within the outermost blob of the polymer layer, in which both the mean-field averaging, and the constitutive relation (3), must break down. Therefore we postulate the existence of a step discontinuity in $f(x)$ at some value x_c , with $f = 0$ for $x > x_c$. (This sharp step, and corresponding features in h and g , would in reality be spread over the a scale $\sim H(t)^{1/2}$, the size of an outermost blob.) This ansatz is enough to determine the scaling functions f, g, h uniquely, including the value of x_c [15], although in practice it is hard to obtain an accurate numerical value; our best estimate is $x_c = 12 \pm 2$. Numerical results from eq. (7) for $f(x)$ and $g(x)$ are shown alongside the simulation data in figs. 3. Since $H(t)$ can be

extracted directly from the data, there is no ambiguity on the horizontal scale, but the parameter values ($k, l\dots$) are not exactly known for the simulation, so $g(x)$ is normalized vertically by the plateau value at $x = \infty$. On this basis, agreement is good for $g(x)$ and reasonable for $f(x)$. The vertical scaling could be avoided by estimating parameter values in the simulation; agreement remains acceptable [15].

We now discuss the validity of the adiabatic approximation ($\partial_t u \ll D\Delta u$) used in eqn. (2) (see [7]). By substituting the scaling results derived above (restoring dimensional factors), we find that this assumption is selfconsistent for short times, but breaks down when the layer reaches a crossover height $h^* \approx (D/kl)^{\epsilon/(1+\epsilon)} g_\infty^{-(1+\epsilon)}$. This can be made arbitrarily large by taking the limit of small incident flux and/or rapid diffusion. For experimental purposes, it may anyway be more realistic to impose, instead of a constant flux, an asymptotic density of the free monomers in the bulk. This would entail a second characteristic length (the depletion length $\xi_D \sim \sqrt{Dt}$ of the incident diffusers). So long as $h \ll \xi_D$, the incident flux is $j_\infty \propto u_\infty \sqrt{D/t}$, and the layer mass M increases as \sqrt{t} rather than linearly. Expressed in terms of M , however, the structural scaling exponents α and β should be unaffected. Once again, the theory will break down at long times.

We have shown how the case of diffusion-limited in-situ polymerization of a polymer brush can be viewed as one of a large class of problems, related to needle-growth models [5,6,8,9], each characterised by an exponent ϵ ; $\epsilon \simeq 2/3$ for polymerization in a good solvent whereas $\epsilon = 1$ recovers the needle growth limit. We found that the scaling exponents for the density, end density and free monomer density obey $\alpha = \epsilon, \beta = 2, \gamma = 1$. These scaling predictions are consistent with detailed Monte-Carlo simulations based on the bond-fluctuation model. This is not obvious because of the coarse-graining implicit the continuum description – which appears to be especially delicate in the outermost blobs of the layer (*cf.* our discussion of $f(x)$ near $x = x_c$). An important extension of our work is to the case of polymerization onto a spherical colloidal particle [3]. We intend to discuss this in a future paper, along with results for flat layers in $d = 2$ [15].

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